

## Understanding of Promoted Hydrate Formation via Interfacial Property Changes

Jae W Lee<sup>C, S</sup>

*The City College of New York, Department of Chemical Engineering, New York, NY, U.S.A.*

*lee@che.ccny.cuny.edu*

Gas hydrates are one branch of clathrate hydrates consisting of host water and guest molecules. The presence of high-pressure guest gas induces a three-dimensional network of hydrogen-bonded water cages, while water molecules frozen into the ice Ih phase do not have any cage structure [1-3]. Between guest gas and water molecules, van der Waals forces usually dominate. Gas hydrates were first discovered by Davy in 1810 [4]. Since then, interest in the study of hydrates focused on preventing hydrate formation because the hydrates plugs formed inside gas/oil pipe lines cause to interrupt the continuous production, resulting in serious safety issues and economical losses. Their importance was again highlighted by the discovery of natural gas hydrates as a potential energy source [5]. They are abundant in marine and arctic sediments and store an immense amount of natural gas. It was estimated that the current natural gas reserve in the hydrate sediments is around 10,000 gigatons [5]. On the other hand, gas hydrates are one of excellent gas storage media, providing a high gas storage density. For example, one unit volume of natural gas hydrates can contain over 170 volumes of natural gas at the standard condition [1-3]. This storage capacity corresponds to about 25 % of the volumetric capacity of liquefied natural gas and is equivalent to compressed natural gas at a pressure of 170 bars.

Despite of their potentials, gas hydrate systems have not been implemented in industry yet due to extremely slow formation kinetics. Gas hydrates are usually formed at the interface between the bulk gas and water phases. Once the solid hydrates cover the interface, gas hydrate formation decreases significantly because the hydrate layer becomes a barrier for mass transfer, and thus hydrate conversion is very low even with several days' hydrate growth. To overcome this problem, people have employed a small amount of surfactants and the gas hydrate formation was accelerated several hundred times faster than water/gas systems [6]. This talk will clarify which mechanism of promoted hydrate formation is dominant, 1) SDS micellization or 2) SDS adsorption to water-hydrate interfaces. The SDS solubility data in hydrate forming temperatures (0 – 8 °C) will be used to explain that the Krafft temperature is not shifted to this low temperature range and SDS molecules do not form micelles [7]. SDS adsorption to water-hydrate interfaces will be confirmed by surface charge and pyrene fluorescence measurements in tetrahydrofuran and cyclopentane hydrate systems that have the same sII structure as natural gas hydrates [8, 9]. The SDS adsorption has been quantified in terms of SDS isotherms [10]. Once SDS molecules adsorb onto the interface, they change water structure to form hydrate clusters in the vicinity of tails and at the same time, loosening hydrogen bonding (water-like feature) on the hydrate surface, which has been observed in Raman and ATR-IR investigations [11-12]. Forming hydrate clusters is supposed to facilitate nucleation while the water-like feature at the interface reduces a diffusion limitation of hydrate formers, resulting in extended hydrate growth.

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